PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improved Process of High Vacuum Distillation

We, EASTMAN KODAK COMPANY, a Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, State of New York, United States of America, (Assignees of KENNETH CLAUDE DAVENPORT HICKMAN, a British Subject, of Kodak Park, Rochester, County Monroe, State of New York, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to an improved process for the vacuum distillation of organic substances such as vegetable and animal oils, fats and waxes containing vitamins, sterols or hormones and which are liquid at the temperature of distillation.

Processes of high vacuum distillation are known in which difficultly volatile materials are removed in purer form from impurities and undesirable admixtures. Thus in U.S. patent to Burch 1,955,321, difficultly volatile oils are vacuum distilled to remove desired constituents therefrom. In U.S. patent No. 1,925,569, natural oils and fats are vacuum distilled to concentrate compounds of therapeutic value contained therein, such as vitamins.

In such high vacuum distillation processes, due to the difficultly volatile nature of the compound being purified, temperatures considerably above the boiling point of the desired compound under the vacuum obtaining must be used. A satisfactory removal of the desired compound at temperatures lower than those heretofore found necessary is of considerable importance, since it would result in a material saving in material otherwise lost due to decomposition. The amount of heat required to volatilize the desired material would also be considerably less.

The present invention has for its object to overcome the deficiencies of hitherto known processes for concentrating or purifying materials by distillation at high vacua, (not more than 1 mm. Hg. and preferably less than 0.1 mm. Hg.) and to provide a process whereby such materials may be purified without undesirable decomposition and with a considerable saving in time and heat energy. It has already been proposed to isolate the female sex hormone by the high vacuum-shortpath distillation of placenta dispersed in oil, i.e. a solid dispersed in a liquid.

According to the present invention the organic substance, such as an oil, fat or wax, which contains vitamins, sterols or hormones and which is liquid at the temperature of distillation is mixed with a compound or mixture of compounds having a boiling point, under the distillation conditions obtaining, in the neighbourhood of that of the material which it is desired to purify, the added material is then preferably removed from the mixed distillate.

When the materials being concentrated or purified are distilled, it has been noticed that temperatures considerably above the boiling point of the desired material must be used. Thus, in distilling fish oils, such as cod liver oil, the vitamins distill over at temperatures varying from 140° to 220° C., the optimum temperature for recovery of vitamin A being about 180° C. Recently nearly pure vitamin A has been secured and it has been found that it distills at less than 100° C. under molecular distillation conditions, i.e. those conditions of high vacuum short path distillation in which the short path referred to is equal to or less than the mean free path of the molecular of the substance being distilled. It is, therefore, seen that it is necessary according to known processes to use a temperature of about 80° C. above the boiling point of the vitamin to eliminate it from the distillate.

If a material having a boiling point in the neighbourhood of that of the desired distillate is added to the mixture to be distilled, it is found that a considerably lower temperature can be used for optimum results. Thus, on vacuum distilling animal and vegetable oils to concentrate fat soluble and other vitamins

contained therein, the addition of a quantity of other material having approximately the same boiling point under vacuum conditions as the desired vitamin, makes it possible to readily distill the vitamin, using a much lower temperature than previously possible.

The use of such lower temperatures is a very desirable feature where heat sensitive and easily decomposable materials are to be recovered. Furthermore, many of the desired distillates are solid or so viscous as to collect in the still and are difficult to remove. The addition of a liquid material having a boiling point in the neighbourhood of the boiling point of the desired distillate will prevent such clogging and make continuous operation possible. Thus, the addition of fatty acids boiling in the neighbourhood of sterols being distilled from an oil prevent the solid or viscous distillate from clogging the apparatus with resultant delay for cleaning.

The materials to be added may be selected from widely different types of compounds or mixtures thereof. Any material may be used as long as it has a boiling point in the neighbourhood of the distillate desired, under molecular distillation conditions as hereinbefore defined and has no adverse effect on the material undergoing treatment. Thus, for example fatty acids, estars, mineral oil fractions, terpenes, essential oils, have been found to give useful results. Of course, a compound which is subject to material decomposition should not be selected. Aliphatic phthalates, benzyl phthalate, beta phenyl ethyl phthalate, diglycerol tetrapropionate boil below vitamin A and are useful agents to employ in its recovery.

Many of the added materials are so expensive that they cannot be used without careful recovery. The distillates containing the added material and the vitamin or other material distilled may be run through a separate still where the vitamin or other desired material may be separated. The added material will remain as the still residue, if it had a higher boiling point than the desired purified material, or will be in the distillate, it has a lower boiling point. In this way the added material can be recovered practically quantitatively. The added material may still contain small amounts of the desired purified material, but as they are used repeatedly, being added again and again to the fresh material initially treated, this does not represent a loss. Obviously other methods of separation known in the art, such as freezing, crystallization, solvent extraction or purely chemical means may be employed instead of distillation for separating the added materials.

As previously indicated, the added material may have a boiling point the same as, above or below that of the substance to be removed. Preferably an added material having a boiling point below that of the desired substance is used, since the lower boiling material generally gives better results at lower temperatures.

As pointed out above, the invention is applicable to any process of high vacuum distillation in which a difficultly volatile organic material is separated as the distillate. Thus, vitamins A, D and/or E may be separated by distillation from vegetable and animal oils containing them, such as cod, halibut, etc. liver oils, menhaden, salmon, dogfish, swordfish, cod, wheat germ oils and the like. Hormones of various types may be recovered from oily concentrates by the present invention, as may also sterols and high boiling hydrocarbons from mixtures containing them.

The distillation may be carried out in the manner described in U.S. patents Nos. 1,925,559 and 1,942,858. Such molecular distillation processes are generally carried out at less than .1 mm. and at temperatures between 70° and 250° C. preferably between 90 and 200° C. A characteristic of this type of distillation is that the vapours are condensed upon a surface located at a distance of less than about the mean free path of the molecules of residual gas. Pressures of above .1 mm. may be used and it has been found that volatile materials in fish oils may be distilled at pressures as high as 1. mm. Since a more economical removal of non-volatile constituents takes place at pressures below .01 mm. we prefer to operate at these lower pressures. However, as the added materials used enable a rapid recovery of the desired materials, it is not necessary in many cases to operate under molecular distillation conditions and pressures higher than those normally used in such processes may be employed, in which case the process may be termed one of pseudo-molecular distillation.

We will now describe our invention by way of example as applied to a fish oil containing vitamins A and D.

We have found in our researches that, although pure vitamin A is an alcohol, the vitamin A occurring in fish oils and highly prized for its medicinal value is a mixture of esters with only a small proportion of the free alcohol. The alcohol boils at about 95° C. and the esters at

160° to 190° C. under a molecular vacuum. The vitamin D from these oils boils at around 140° C. When, however, it is desired to drive the vitamins off from the parent oil, it is found that temperatures of 160° C. and higher are required for the D and 180° to 215° C. for the A. This is partly because the vitamins are present in such minute quantities and partly because there are only relatively small amounts of fatty glycerides in the oil of boiling points similar to the vitamins. The oil of commerce is rich in the long chain fatty glycerides, and comparatively rich in free fatty acids, but the fatty glycerides with 8 to 14 carbon atoms in the side chain are conspicuous by their absence. We therefore add, for instance, to the incoming oil four parts of glycerol tripelargonate (tri-pelargonin) and we then find that distillation of a fraction rich in A and D occurs at a temperature of 160° C. The quantity of the fraction is about 5%.

The added material, e.g. tripelargonin, serves another important purpose, in that it condenses with the desired fraction and thus increases its bulk so that it flows away more readily from the solid condensing surface. Our researches have shown that the distillation characteristics of Vitamin D and cholesterol are very similar. The vitamin D when ordinarily eliminated has so small a bulk that it takes a long time to drain from the condensing surface and often suffers decomposition on the way. With oils rich in cholesterol, the vitamin is held on the condensing surface in a mass of crystals. In melting these down, the vitamin D is volatilised and partly decomposed. It will be appreciated that when tripelargonin or is equivalent is added, the bulk of the condensate is increased, the crystallisation of the cholesterol is prevented, or minimized, and the vitamins are swept rapidly from the still. Materials which have an appreciable solvent action on the distillate are preferred though those having slight or partial solvent action can be used.

It is not known how the agents used effect the results described but they lower the effective temperature at which distillation is practicable.

The added material appears to act as a diluent which creates a vigorous vapour stream to sweep along the distillate with it in the same fraction. When a material of somewhat lower boiling point is added, it may assist in preventing the sluggish molecules of distillate material from returning to the liquid being distilled. This effect is particularly important in pseudo-molecular distillation where the molecules are condensed on a surface which is at a greater distance than the mean free path of the molecules.

The herein described invention constitutes a simple, economical and highly effective solution of the problem of removal by vacuum distillation of difficulty volatile organic compounds and particularly of heat sensitive difficultly volatile compounds from mixtures containing them. An outstanding advantage of our process is the more rapid distillation at lower temperatures than could heretofore be used and the possibility of distilling solids without clogging of the apparatus.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the process of distillation of organic substances, which are liquid at the temperature of distillation and which contain vitamins, sterols or hormones, to separate a desired fraction at a high vacuum of not more than 1 mm. Hg, the step which comprises adding to the organic material to be distilled a substance of low volatility, which distils over as a mixed distillate with a desired fraction.

2. The process as claimed in claim 1 applied specifically to those substances which are liquid at or near atmospheric temperature.

3. The process as claimed in claim 1 in which a natural oil containing vitamins, sterols or hormones is distilled in presence of an added material which distils with the desired fraction, after which the added material is separated from the mixed distillate.

4. The process as claimed in claim 1 applied to the separation of vitamin, sterol or hormone concentrates from material containing one or more of these therapeutic substances, the distillation being performed under molecular conditions as hereinbefore defined.

5. The process as claimed in claim 1 which comprises adding to a substance to be vacuum distilled a material having a boiling point in the neighbourhood of the desired fraction and subjecting the mixture to vacuum distillation.

6. The process as claimed in claim 1 which comprises adding to a natural oil a substance having a boiling point near that of the desired fraction and subjecting the mixture to distillaion at a pressure of less than 0.1 mm. and a temperature between 70 and 250° C. and condensing the distillate at a distance from

the evaporative surface of less than the mean free path of the molecules of residual gas.

7. The process as claimed in any of the preceding claims in which the added material is more volatile than the desired fraction.

8. The process as claimed in any of the preceding claims in which the distillation is performed at pressures less than 0.1 mm. Hg.

9. Processes of high vacuum distillation, substantially as described.

Dated this 9th day of October, 1936.

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Chartered Patent Agents.

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